Structure of Amines

• Nitrogen atom of amino group is *sp*³ hybridised. Three of these orbitals get involved in sigma bond formation with other atoms whereas fourth orbital contains lone pair of electrons. Thus amines are pyramidal in shape.



Orbital structure of 1°, 2• and 3° amines

General Methods of Preparation

- From alcohols : $CH_3CH_2OH \xrightarrow{NH_3, \Delta} CH_3CH_2NH_2 \xrightarrow{CH_3CH_2OH, \Delta} -H_2O$ Primary amine $(CH_3CH_2)_2NH \xrightarrow{CH_3CH_2OH, \Delta} (CH_3CH_2)_3N$ Secondary amine
- Gabriel phthalimide synthesis : For converting alkyl halides to primary amines.





• Hofmann bromamide reaction : For converting amides to primary amines having one carbon atom less.

$$H_{3}C - C - NH_{2} \xrightarrow{Br_{2}} CH_{3}NH_{2} + K_{2}CO_{3} + KBr + H_{2}O$$

Acetamide

• Reduction of N-containing compounds :

 $\begin{array}{c} CH_{3}CH_{2}NO_{2} & \xrightarrow{Sn/HCl \text{ or } H_{2}/Pt} & CH_{3}CH_{2}NH_{2} \\ \hline \\ Nitroethane & Ethanamine (Primary amine) \\ \\ CH_{3}CH_{2}CN & \xrightarrow{LiAlH_{4} \text{ or } Na/alcohol} & CH_{3}CH_{2}CH_{2}NH_{2} \\ \hline \\ Ethyl \text{ cyanide} & Propanamine (Primary amine) \end{array}$

$$\begin{array}{c} \text{CH}_{3}\text{CONH}_{2} \xrightarrow{\text{LiAIH}_{4}} & \text{CH}_{3}\text{CH}_{2}\text{NH}_{2} \\ \text{Ethanamide} & \text{Ethanamine}(\text{Primary amine}) \end{array}$$

By hydrolysis of N-containing compounds :

CH₃CH₂NC $\xrightarrow{H^+/H_2O}$ CH₃CH₂NH₂ Ethyl isocyanide CH₃CH₂NH₂

$$CH_{3}CH_{2}N = C = O \xrightarrow{KOH} CH_{3}CH_{2}NH_{2}$$

Ethyl isocyanate Ethanamine

 Schmidt reaction : To convert carboxylic acid to amines having one carbon atom less.

$$CH_{3}COOH \xrightarrow{N_{3}H, \Delta} CH_{3}NH_{2} + CO_{2} + N_{2}$$

$$COOH \qquad \qquad NH_{2}$$

$$H_{2}SO_{4} \qquad \qquad NH_{2}$$

$$H_{2}SO_{4} \qquad \qquad H_{2}SO_{2} + N_{2}$$
Benzoic acid
$$Aniline$$

Ritter reaction :

$$\begin{array}{c} \begin{array}{c} CH_{3} \\ H_{3}C - \begin{array}{c} - \begin{array}{c} CH_{3} \\ - \begin{array}{c} OH \\ - \end{array} \end{array} \\ \begin{array}{c} (i) HCN, H_{2}SO_{4} \\ (ii) H^{+}/H_{2}O \end{array} \end{array} \hspace{0.5cm} H_{3}C - \begin{array}{c} CH_{3} \\ - \begin{array}{c} OH_{3} \\ - \end{array} \\ \begin{array}{c} OH_{3} \\ - \end{array} \\ \begin{array}{c} OH_{3} \\ OH_{3} \end{array} \end{array}$$

Physical Properties

- Lower amines are gases and liquids but higher amines are solids.
- Primary and secondary amines have higher boiling points than other organic compounds due to hydrogen bonding.
- Primary and secondary amines are soluble in water due to hydrogen bonding between -NH₂ and H₂O molecules.

Basic Character

The amines are basic in nature due to the presence of a lone pair of electron on N-atom of the $-NH_2$ group, which it can donate to electron deficient compounds. Aliphatic amines are stronger bases than NH_3 because of the +*I* effect of the alkyl groups. Greater the number of alkyl groups attached to N-atom, higher is the electron density on it and more will be the basicity. Thus the order of basic nature of amines is expected to be $3^{\circ} > 2^{\circ} > 1^{\circ}$, however the observed order is $2^{\circ} > 1^{\circ} > 3^{\circ}$. This is explained on the basis of crowding of N-atom of the amine by alkyl groups which hinders the approach and bonding by a proton, consequently, the electron pair which is present on N is unavailable for donation and hence 3° amines are the weakest bases.

The order of basicity varies with the nature of alkyl group.

Alkyl group	Basic strength
CH_3 -	$R_2 NH > RNH_2 > R_3 N > NH_3$
$C_{2}H_{5} -$	R_2 NH > R_3 N > R NH ₂ > NH ₃

Aniline is a weaker base compared to ammonia. This is because the lone pair of electrons on N-atom of aniline is less available for protonation due to its involvement in conjugation with the π -electrons of the benzene ring.



Further the presence of electron withdrawing groups like $-NO_2$, -CN, -X, etc., decreases the basicity while, the presence of electron donating groups like -OCH₃, -CH₃, -NH₂, etc., activates the benzene ring and also increases the basicity.

Chemical Properties

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- **Oxidation**: $RCH_2NH_2 \xrightarrow{KMnO_4} RCH = NH \xrightarrow{H_2O} RCHO + NH_3$ R_2 CHNH₂ $\xrightarrow{\text{KMnO}_4} R_2$ C=NH $\xrightarrow{\text{H}_2\text{O}} R_2$ CO + NH₃ $R_3 \text{CNH}_2 \xrightarrow{\text{KMnO}_4} R_3 \text{CNO}_2$
- **Electrophilic substitution reactions :** $H_2O \longrightarrow RNH_3^+OH \longrightarrow RNH_3^+ + OH$ $\frac{\text{HCl}}{\Rightarrow} R \text{NH}_2 \cdot \text{HCl} \text{ or } R \text{NH}_3^+ \text{Cl}^ AgCl \rightarrow [Ag(RNH_2)_2]^+Cl^ \frac{RI}{-HI} \stackrel{R}{\xrightarrow{}} R_2 NH \xrightarrow{RI} -HI \stackrel{R}{\xrightarrow{}} R_3 N \xrightarrow{+RI} \stackrel{R}{\xrightarrow{}} R_4 NI \xrightarrow{-AgOH} -AgI R_4 N^+ OH^$ tetraalkyl ammonium iodide (exhaustive alkylation) RCOC1 RNHCOR + HCl (substituted amide) RNH; RNHCOR + RCOOH RCHO, H⁺ $RN = CHR + H_{2}O$ Schiff's base or anil CHCl₃, 3KOH (alc.) $RNC + 3KC1 + H_2O$ warm Alkyl isocyanide [where $R = alkyl \text{ or aryl}, Carbylamine reaction}]$ $R'-H + Mg < \frac{NHR}{V}$ R'MgX CS₂, HgCl₂ $RNC \equiv S + HgS + 2HCl$ Δ Alkyl isothiocyanate [Hofmann's mustard oil reaction] COCl₂ -NH - C - NH - R + 2HC1sym-disubstituted urea **Reaction** with nitrous acid :

$$\frac{RNH_2}{(1^{\bullet})} \xrightarrow{HNO_2} ROH + N_2 + H_2O$$

$$R_{2}NH \xrightarrow{HNO_{2}} R_{2}N - N = O \xrightarrow{C_{6}H_{5} \oplus H}_{conc. H_{2}S \oplus_{4}} \text{ green soln.}$$
(2*) Nitrosoamine
(yellow oil)
$$\xrightarrow{H_{2}O} \text{ red solution } \xrightarrow{NaOH}_{} \text{ blue}$$

$$Liebermann's \text{ nitroso reaction}$$

$$R_{3}N \xrightarrow{HNO_{2}} [R_{3}NH]^{+}NO_{2}^{-} \xrightarrow{\Delta} R - OH + R_{2}N - N = O$$
3° amine Trialkylammonium Alcohol Nitrosoamine
nitrite
Cope elimination :

C₆H₅●H

CH. CH - N - CH, N – CH₃

Dimethylisoproj

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Hoffman elimination reaction : In this there is formation of an olefin by pyrolysis of a quaternary ammonium salt.

$$\begin{bmatrix} CH_{3} \\ H_{3} - N - C_{2}H_{3} \\ CH_{3} - N - C_{2}H_{3} \end{bmatrix} OH^{-} \xrightarrow{\Delta}_{400 \text{ K}} CH_{3} - N + H_{2}C = CH_{2} + H_{2}O \\ CH_{3} - N - C_{4}H_{3} \\ CH_{3} - N - C_{2}H_{3} \\ CH_{3} - N - C_{2}H_{3} \\ OH^{-} CH_{3} + CH_{3} - N + H_{2}C = CH_{2} + H_{2}O \\ CH_{3} - N + H_{2}C = C_{6}H_{5} - NHCO - C_{6}H_{5} \\ NaOH \\ (Schotten - Baumann reaction) \\ NaNO_{2}, HCl \\ 0 - 5^{\circ}C + C_{6}H_{5} - N_{2}^{+}Cl^{+} \\ CS_{2} \\ CS_{2} \\ CG_{6}H_{5} - NH_{2}CS \\ Diphenyl thiourea \\ Br_{2} \\ 2,4,6 - Tribromoaniline \\ C_{6}H_{3}NH_{2} \rightarrow Conc. H_{2}SO_{4} \\ H_{2}N - O - SO_{3}H \\ \hline \\ conc. HNO_{3} \\ conc. H_{2}SO_{4} \\ H_{2}N - O \\ NO_{2} \\ K_{2}Cr_{2}O_{7}H^{+} \\ O - O - O \\ \hline \\ D \\ P-Benzoquinone \\ \hline \\ H_{2}SO_{5} \\ \hline \\ O \\ \hline \\ O \\ \hline \end{bmatrix}$$
 Nitrobenzene